

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-003466

(43)Date of publication of application : 09.01.2002

(51)Int.Cl.

C07C303/02
C07C309/13
H01B 1/06
H01B 13/00
H01M 8/02
H01M 8/10
H01M 10/40
// C07D251/24

(21)Application number : 2000-189621

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(22)Date of filing : 23.06.2000

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(54) NEW FLUORINE-CONTAINING COMPOUND AND METHOD FOR PRODUCING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a fluorine-containing nitrile compound containing a sulfonic group and a cyano group and to provide a method for producing the same.

SOLUTION: A compound represented by formula $\text{FSO}_2\text{CF}_2[\text{CF}_2\text{OCF}(\text{CF}_3)]_n\text{CN}$ ((n) is 0, 1, 2 or 3) is hydrolyzed in the presence of a tertiary amine and brought into contact with an acid type ion exchange resin to give the fluorine-containing nitrile compound represented by formula $\text{HOSO}_2\text{CF}_2[\text{CF}_2\text{OCF}(\text{CF}_3)]_n\text{CN}$ ((n) is 1, 2 or 3).

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

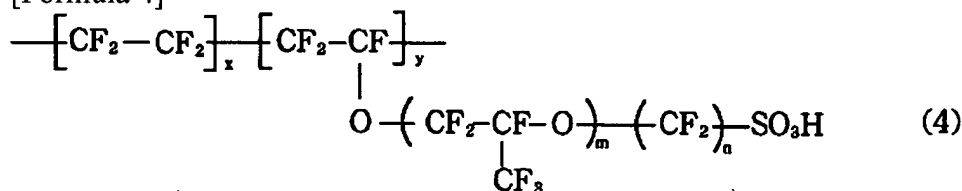
[Field of the Invention] This invention relates to the new fluorine-containing nitril compound containing a sulfonic group (-SO₃H), and its manufacture approach.

[0002]

[Description of the Prior Art] Conventionally, in the field of a fuel cell, the perfluorocarbon polymer (a perfluorocarbon-sulfonic-acid polymer is called hereafter.) of the sulfonic group content which has the structure of a formula (4) as the film and a proton conductor of a catalyst bed is mainly used.

[0003]

[Formula 4]



[0004] (As the inside of a formula, and x, comparatively, x:y is about 20:1-2:1 and m is an integer of y whose n is 1-12 in 0, 1, or 2.) [0005] This copolymer is CF₂=CF₂. CF₂=CFO [CF₂CF(CF₃)O] After obtaining the copolymer which carries out radical copolymerization of m (CF₂)_n SO₂F, and has a fluoro sulfonyl group (-SO₂F) at the end of a side chain and hydrolyzing this fluoro sulfonyl group by the base, it is compounded by carrying out the ion exchange with proton acid. Usually, the polymer of m= 1 and n= 2 is used.

[0006] On the structure, since the above-mentioned perfluorocarbon-sulfonic-acid polymer did not contain any hydrogen, it is physical very [chemically and] stable, and can operate a fuel cell at comparatively high temperature, and its cell engine performance improved substantially. A deer is carried out, and as for a fuel cell, operating in an elevated temperature further is desirable in order to reduce the catalyst poisoning by the carbon monoxide contained in the hydrogen gas of a fuel. However, since this is a polymer non-constructing a bridge although the configuration is held with the par FURUO carbon chain when the above-mentioned polymer is formed in the film etc., the reinforcement and endurance in an elevated temperature have the technical problem that there is nothing, if not necessarily enough.

[0007] Although it was thought suitable to use the perfluorocarbon-sulfonic-acid polymer over which the bridge was constructed fundamentally in order to conquer the above-mentioned technical problem, the available bridge formation perfluorocarbon-sulfonic-acid polymer was not known industrially conventionally.

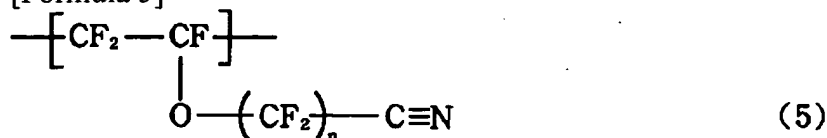
[0008] On the other hand, as a perfluorocarbon polymer which can construct a bridge, it is a side chain. - It is CN. The polymer which has a radical is well-known (see JP,6-340710,A etc.).

[0009] formula which specifically has the following repeat unit (5) ** (6) The perfluorocarbon polymer

expressed is illustrated.

[0010]

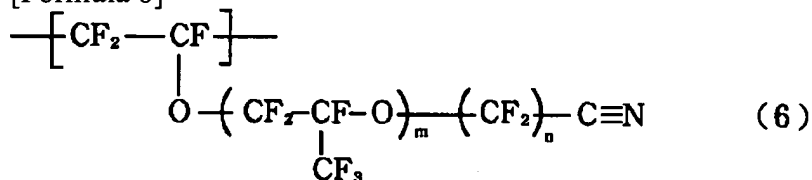
[Formula 5]



(The inside of a formula, integer of n=1-12)

[0011]

[Formula 6]

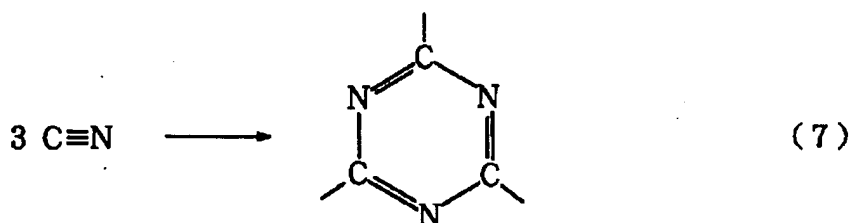


(The inside of a formula, integer of m= 1 and 2 n=1-4)

[0012] Inside of the compound expressed with the above-mentioned formula - CN It is a formula, using a radical as a catalyst for tetra-phenyl tin, triphenyltin hydroxide, Zn (C₇F₁₅CO₂)₂, Co (C₇F₁₅CO₂)₂, 1-perfluoro octane sulfonic acid, 2-ethylhexylamine, an aniline, etc. (7) A bridge formation perfluorocarbon polymer is formed by making a triazine ring generate by 3 quantification reactions.

[0013]

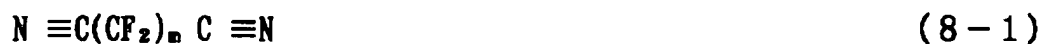
[Formula 7]



They are two pieces to intramolecular further again. - CN A bridge formation perfluorocarbon polymer can be obtained also by performing the reaction same about the perfluorocarbon compound which has a radical (for example, United States patent No. 3,317,484). They are two pieces to this intramolecular. - CN The compound concretely shown in following type (8-1) - (8-5) as a perfluorocarbon compound which has a radical is illustrated, and especially the boiling point can use a thing higher than near a room temperature suitably in these.

[0014]

[Formula 8]



(式中、 $n = 2 \sim 12$ の整数)



(式中、 $n = 0 \sim 12$ の整数、 $X = F$ 又は CF_3)



(式中、 $n = 2 \sim 12$ の整数、 $X = F$ 又は CF_3)



(式中、 $n = 0 \sim 12$ の整数、 $y = 0 \sim 100$ の整数、 $X = F$ 又は CF_3)



(式中、 $n = 2 \sim 12$ の整数、 $u+w = 0 \sim 100$ の整数、 $X = F$ 又は CF_3)

therefore, if the perfluorocarbon polymer which has -SO₃H radical, or the perfluoro compound which has two or more -CN radicals like formula (8-1) - (8-5) is mixed and crosslinking reaction is made to perform, it will be thought that the bridge formation perfluorocarbon polymer containing a sulfonic group is obtained. A radical and -CN the perfluorocarbon compound which has both radicals -- compounding -- formula (5) ** (6) like -- a side chain -CN

[0015] However, -SO₃H Radical - CN The perfluoro compound which has both radicals is not known conventionally.

[0016]

[Problem(s) to be Solved by the Invention] This invention has a sulfonic group and a cyano group, and it is useful as an electrolyte in itself, and it aims at offering the new fluorine-containing compound and its manufacture approach of reference non-** which can perform the triazine ring formation reaction by 3 quantification of a cyano group.

[0017]

[Means for Solving the Problem] It will be a formula if this invention is followed. (1) New sulfonic group content fluorine-containing nitril compound ** expressed is offered.

[0018]

[Formula 9]



(The inside of a formula, $n = 0, 1$ and 2 , or 3)

Moreover, it will be a formula if this invention is followed. (2) [0019]

[Formula 10]



(The inside of a formula, $n = 0, 1$ and 2 , or 3)

[0020] Formula characterized by making acid type ion exchange resin contact after coming out and hydrolyzing the fluoro sulfonyl group of a fluorine-containing compound expressed under existence of tertiary amine (1) Manufacture approach ** of a fluorine-containing nitril compound expressed is offered.

[0021]

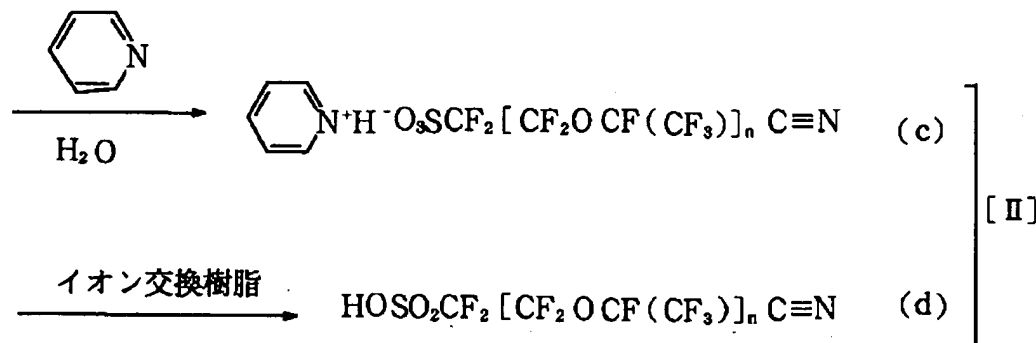
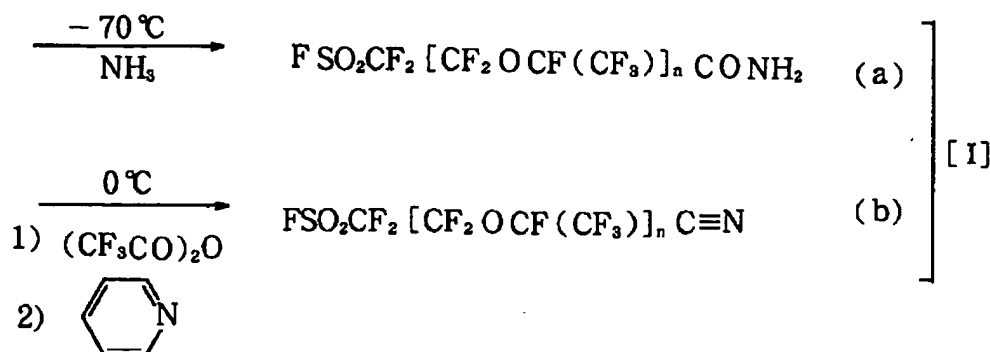
[Embodiment of the Invention] Hereafter, this invention is explained to a detail.

[0022] the fluorine-containing nitril compound of this invention -- for example, the following schemes -

- following -- two steps of reactions -- it is compoundable by [I (a)], (b) and [II] (c), and (d).

[0023]

[Formula 11]



[0024] [I] The reaction of (a) and (b) is a formula. (1) Formula used as the starting material of compound composition of this invention expressed (2) It is the reaction which compounds the fluoro sulfonyl group content fluorine-containing compound expressed.

[0025] the carboxylic-acid full ora whose reaction (a) of the preceding paragraph of said fluorine-containing compound used as this starting material is acid halide -- the id -- it is the alternative amidation reaction of the fluoro formyl group (-COF) of a derivative. Specifically, the amidation concerned is a formula (9).

[0026]

[Formula 12]



(9)

(n has the already defined semantics among a formula.)

[0027] It is the fluorine-containing compound (carboxylic-acid full ora id derivative) come out of and expressed in an aprotic solvent and under low temperature NH₃ You make it contact and it is carried out by amidating only a fluoro formyl group selectively.

[0028] NH₃ Formula (9) As for the temperature to which a compound is contacted, it is desirable preferably that it is -80 degrees C - -30 degrees C low temperature -100 degrees C - 30 degrees C in order to raise the selectivity of the amidation about a fluoro formyl group.

[0029] As an aprotic solvent used for a reaction, it is diethylether, tetrahydrofuran, diphenyl ether,

hexane, octane, fluorobenzene, bromobenzene, 2H, and 3H-perfluoro pentane, 1H-perfluoro hexane, 1, and 1-dichloro, for example. - It is 2, 2, 3, 3, and 3-pentafluoro propane, 1, and 3-dichloro. - 1, 1, 2, 2, a 3-pentafluoro propane, dimethylformamide, dimethylacetamide, a methylene chloride a carbon tetrachloride, mono-glyme a jig lime, etc. be used suitably

[0030] NH₃ in order that the amount used may raise the selectivity of amidation -- formula (9) the carboxylic-acid full ora expressed -- the id -- a derivative -- receiving -- a 0.8 to 1.5 time mol -- it is a 1.0 to 1.2 time mol preferably.

[0031] In order to make a fluoro formyl group amidate selectively in this amidation reaction, it is the concentration of a fluorine-containing compound NH₃ It is important to make it react in the superfluous condition to concentration. For that, the whole quantity of a fluorine-containing compound is taught to the reaction container, and it is NH₃. It is desirable to carry out division supply with means, such as dropping, into the fluorine-containing compound concerned.

[0032] Reaction time is reaction temperature and NH₃. Although it may change with a mole ratio, the amount of activity nonprotic solvents (namely, concentration of a reaction solute), etc., it is usually about 1 - 24 hours preferably for 0.5 to 30 hours.

[0033] On the other hand, a latter reaction (b) is a nitril-ized reaction, makes the carboxylic amide generated by the reaction formula (a) in the solvent which aprotic [the / as the case of the above-mentioned amidation / same] dried react with a dehydrating agent, and makes nitril generate.

[0034] The range of -30-100 degrees C of reaction temperature of nitril-izing is -20-60 degrees C preferably. At low temperature, a reaction rate falls not much from this, and when temperature is not much high, it becomes impossible to disregard side reaction from this.

[0035] As a dehydrating agent, the usual dehydrating agent is usable, for example, a phosphorus pentaoxide, an acetic anhydride, a trifluoroacetic acid anhydride, phthalic anhydride, phosphorus oxychloride, a thionyl chloride, etc. are mentioned.

[0036] In addition, in the nitril-ized reaction which uses the dehydrating agent used as an acid after dehydration in this way, it is desirable to make the basic compound which carries out the trap of the acid which carries out a byproduction live together with a dehydrating agent.

[0037] As a desirable basic compound, it is tertiary amine which H atom has not combined with N directly. In this description, tertiary amine shall also contain pyridines and other heterocyclic compounds which do not have N-H coupling other than the 3rd class fatty amine. As an example, a trimethylamine, triethylamine, the Tori (n-propyl) amine, The Tori (i-propyl) amine, the Tori (n-butyl) amine, tripentylamine, Trihexyl amine, a triheptyl amine, Tori (n-octyl amine), The Tori (i-octyl) amine, a TORINO nil amine, a tridecyl amine, TORIUNDE sill amine, tridodecylamine, N, and N-dimethyl-n butylamine, The 3rd class fatty amines, such as an N and N-dimethyl-n-octyl amine, N and N, N', and N'-tetramethylethylenediamine; A TORIBI nil amine, Aliphatic series partial saturation tertiary amine, such as a triaryl amine; Dimethylaniline, diethylaniline, Aromatic series tertiary amine, such as tribenzylamine and a triphenylamine; A pyridine, alpha-methylpyridine (alpha-picoline), beta methylpyridine (beta-picoline), gamma-methylpyridine (gamma-picoline), 2, 6-lutidine (2, 6-lutidine), 2, 4-lutidine (2, 4-lutidine), 2,4,6-trimethylpyridine (2,4,6-collidine), Pyridazine, pyrazine, pyrimidine 1, 5-diazabicyclo [4, 3, 0] -5-nonene, 1, 5-diazabicyclo [4, 3, 0] Non, the heterocycle type tertiary amine containing nitrogen atoms, such as -5-en, N-methyl morpholine, and 1-methyl piperidine, is mentioned. In the above-mentioned scheme, it is the example which is reacting at 0 degree C by using a pyridine as a basic compound.

[0038] Although the amount of the dehydrating agent used may change with the class of dehydrating agent, the amount of the amide which should dehydrate, etc., it is about 1.0-3.0 mols preferably 1.0-5.0 mols per one mol of carbamoyl groups.

[0039] Moreover, although the amount of the basic compound used may change with the class of the basic compound concerned, the amount of a dehydrating agent, etc., it is usually about 1.0-3.0 mols preferably 0.5-4.0 mols to one mol of dehydrating agents.

[0040] Although the reaction time of nitril-izing may change with reaction temperature, a dehydrating-agent mole ratio, the amount of activity nonprotic solvents (namely, concentration of a reaction solute),

etc., it is usually about 1 - 24 hours preferably for 0.5 to 30 hours.

[0041] The carbamoyl group of an amide compound is changed into a cyano group by the above actuation by the reaction (formula (b)) with dehydrating agents, such as a trifluoroacetic acid anhydride and a phosphorus pentaoxide.

[0042] In this way, two-phase separation of the fluoro nitril to generate is carried out to the solvent phase containing the reaction residue with a dehydrating agent and a dehydrating agent as a phase which most becomes from the fluoro nitril concerned. Subsequently, it is possible by dissociating from a solvent phase and rinsing the fluoro nitril content phase concerned with a liquid-liquid separation means, to obtain fluoro nitril by high yield. Usually, eventually, the fluoro nitril of a high grade is isolated by carrying out distillation purification of the fluoro nitril content phase.

[0043] The yield of the fluoro nitril from the fluoro amide by this approach is high, is at least 50% or more, and usually exceeds 70%.

[0044] In addition, it can mix with a dehydrating agent and non-solvents, such as a phosphorus pentaoxide, besides the approach of performing in the nonprotic solvent of the above-mentioned publication, and a nitril-ized reaction can also adopt the approach of heating at 100-300 degrees C.

[0045] [II] (c) and (d) are the formula which are the 2nd step of reaction and were obtained by carrying out like the above. (2) A fluoro sulfonyl group content fluorine-containing compound It is a formula by making acid type ion exchange resin contact like a formula (d), after hydrolyzing the fluoro sulfonyl group (FSO₂-) under existence of tertiary amine according to a formula (c). (1) The sulfonic group content fluorine-containing nitril compound of this invention expressed is obtained.

[0046] In this invention, it is characterized by hydrolyzing under existence of the tertiary amine instead of the alkali like a potassium hydroxide, a sodium hydroxide, and potassium carbonate.

[0047] Especially as tertiary amine, it is not limited and the various tertiary amine indicated in the above-mentioned nitril-ized reaction can be used suitably.

[0048] The amount of the water used for hydrolysis is usually a formula. (2) It is desirable to carry out [stoichiometric] a mol grade activity to a fluoro sulfonyl group content fluorine-containing compound. When hydrolysis is not fully performed when there are few amounts of the water used from this, but not much superfluous water is used from this, hydrolysis of a cyano group will be induced and it is not desirable.

[0049] In this invention, hydrolysis of a fluoro sulfonyl group is performed to the bottom of existence of the above-mentioned tertiary amine (in the above-mentioned scheme, it is the example which is using the pyridine as tertiary amine.). Although HF is emitted along with progress of hydrolysis and a sulfonic group is formed (H₂O+FSO₂- → HF+HOSO₂-), while tertiary amine catches this emitted HF, it is thought in this invention that the generated sulfonic group is neutralized. That is, if tertiary amine is expressed with NR¹R²R³ (R¹-R³ shows alkyl etc.), for example, it will be thought that this is expressed with the reaction formula of the following (10) and (11).

[0050]

[Formula 13]



[0051] For that, the amount of the tertiary amine used is a fluoro sulfonyl group content compound at least. (2) It receives and it is usually desirable a two to 15 time mol and that it is a three to 10 time mol preferably.

[0052] -50-30 degrees C of temperature of hydrolysis are about -30-10 degrees C preferably. Since a hydrolysis reaction advances comparatively easily, it is desirable for it not to be necessary to carry out by warming not much, and to carry out at the temperature of above-mentioned extent also from the point of preventing side reaction. Although reaction time may change also with reaction temperature, it is

usually about 1 - 4 hours preferably for 0.5 to 24 hours.

[0053] Especially as equipment for carrying out a hydrolysis reaction, although it does not limit, the reaction container of the mixing vessel mold equipped with an agitator, a thermometer, heating/cooling system, a temperature controller, water and/or the dropping equipment of tertiary amine, or a weight or volumetric or counting feeder is desirable. Moreover, it can also consider as successive reaction actuation with the reaction container of a juxtaductal type.

[0054] As a solvent which hydrolyzes, it is desirable to use an aprotic solvent. For example, a tetrahydrofuran (THF), diethylether, diphenyl ether, Methyl-t-butyl ether, dioxane, an anisole, diphenyl ether, Methyl ether, ethyl ether (perfluoro butyl), (Perfluoro butyl) Ether, such as mono-glyme, a jig lime, a TORIGU lime, and tetraglyme; A hexane, Aromatic hydrocarbon, such as hydrocarbon; benzene, such as a heptane and an octane, toluene, and a xylene; A fluorobenzene, Halogenated-aromatics hydrocarbon; 2H, such as a bromobenzene, a chlorobenzene, and a dichlorobenzene, a 3H-perfluoro pentane, A 1H-perfluoro hexane, a 1H-perfluoro octane, a 1H-perfluoro decane, 1H and 4H-perfluoro butane, 1H, 1H, 1H and 2H, a 2H-perfluoro hexane, 1H, 1H, 1H, 2H, a 2H-perfluoro octane, 1H, 1H, 1H and 2H, a 2H-perfluoro decane, 3H and 4H-perfluoro (2-methyl pentane), 2H, and 3H-perfluoro (2-methyl pentane), 1 and 1-dichloro - 2, 2, 3, 3, and 3-pentafluoro propane, 1, 3-dichloro - 1, 1, 2, 2, a 3-pentafluoro propane, 1 and 1-dichloro-1-fluoro ethane, perfluoro (2-butyl tetrahydrofuran), 3 and 3-dichloro - 1, 1, 1, 2, and 2-pentafluoro propane, In addition to this, Fluoroalkane compounds, such as 1,1,2-trichloro-1,2,2-trifluoroethane and a perfluoro octane; An acetone, Dimethylformamide, dimethylacetamide, dimethyl sulfoxide, Although hexamethylphosphoramide, a sulfolane, an acetonitrile, ethylene carbonate, propylene carbonate, gamma-butyrolactone, chloroform, a methylene chloride, a carbon tetrachloride, etc. can be used suitably These are only instantiation and are not limited to this.

[0055] although the water and tertiary amine which are used for a hydrolysis reaction may also teach the whole quantity to a reaction container by package -- dropping equipment or a metering pump -- using it - - the system of reaction -- serially -- addition or continuation addition -- carrying out -- making -- reaction temperature -- the above -- it is also desirable to advance a reaction, controlling to become a desirable temperature requirement. Moreover, when using a juxtaductal type reaction container, temperature control, i.e., control of a reaction rate, can also be performed by preparing the feed hopper of water and tertiary amine in each part of a coil, and carrying out division installation of water and the tertiary amine from this feed hopper.

[0056] In this invention, the reaction solution after hydrolysis is contacted to solid acid, and it is a formula. The sulfonic group content fluorine-containing nitril compound expressed with (1) is made to separate. although a salt generates when an acid is made to contact, in order [usually,] to make separation with this salt easy -- an acid -- solid acid -- a macromolecule acid is used preferably. It is using acid type ion exchange resin preferably especially.

[0057] Although all are usable if acid type ion-exchange resin is insoluble in the water which introduced the sulfonic group, the carboxyl group, the phenolic hydroxyl group, etc. into parent synthetic resin, such as polystyrene which constructed the bridge by a small amount of divinylbenzene, the thing of strong acid nature is desirable and the thing containing especially a sulfonic group is desirable.

[0058] Although it may not limit and you may be an infinite form (crushing form) especially as a gestalt of ion exchange resin, the thing of the shape of the shape of a ball or a grain is used preferably.

[0059] moreover -- as particle size -- 180-1700 micrometers -- desirable -- about 250-850 micrometers -- it is -- as ion exchange capacity -- 3 - 7 milliequivalent / g desiccation resin -- the thing of 4.5 - 6.5 milliequivalent / g desiccation resin extent is preferably desirable.

[0060] As for the total capacity of ion exchange resin, it is desirable to use it in consideration of the amount of the tertiary amine used superfluously, so that it may become sufficiently superfluous to this.

[0061] An ion exchange reaction can be advanced various gestalten being possible for the approach of contact on the reaction solution after hydrolysis, and ion exchange resin, for example, feeding a reaction solution and ion exchange resin into a mixing vessel mold container, and making ion exchange resin float under churning. It is the method to which fill up a column type container with ion exchange resin,

form the fixed bed (column) in more preferably, supply a reaction solution from the head of this fixed bed, and the ion exchange is made to perform. The ion exchange is carried out moving in the inside of the packed bed which consists of the ion exchange resin concerned, and the supplied reaction solution is a formula. (1) A sulfonic group content fluorine-containing nitril compound separates.

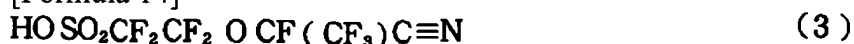
[0062] On the other hand, since tertiary amine is held at the ion exchange resin concerned and does not flow out, it is considered that the whole quantity of the target sulfonic group content fluorine-containing nitril compound contains substantially in the reaction solution which flows out of the column other end.

[0063] The sulfonic group content fluorine-containing nitril compound of this invention supplies the reaction solution which usually carried out ion exchange treatment to a distillation apparatus or concentration equipment in this way, and are collected as bottoms (can residual liquor) of the equipment which carried out distillation separation of the solvent etc.

[0064] Formula by the above reaction (1) The yield of the fluoro sulfonyl compound (formula (2)) criteria of the fluorine-containing nitril compound of this invention expressed is usually 80% or more and high yield at least 70% or more. In addition, formula (1) It is the formula which it sets, and n is 0, 1, 2, or 3, and is a start raw material. (2) Although the number of n of a fluorine-containing nitril compound also becomes settled according to n of a fluorine-containing compound, especially the compound in n=1 (formula (3)) can be obtained most easily. It is a formula here. (3) Fluorine-containing nitril is also the nitril compound compounded in the after-mentioned example.

[0065]

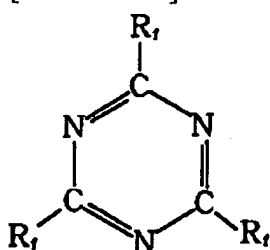
[Formula 14]



[0066] Formula which has the sulfonic group and cyano group of this invention in both ends (1) A fluorine-containing nitril compound is a formula by 3 quantification reactions of the cyano group of an end. (12) It is possible to change into the triazine ring content compound expressed.

[0067]

[Formula 15]



(12)

(n expresses among a formula the semantics which formula (1) already defined.)

[0068] A triazine ring formation reaction can be carried out by the approach that a publication is well-known in itself, to JP,47-17793,B or JP,6-340710,A.

[0069] Namely, a bismuth, copper, lead, barium, cadmium, tin, a thallium, Metal catalysts, such as cadmium and an indium, tetra-phenyl tin, oxidation triphenyltin, Zn (C7 F15CO2)2, 1-perfluoro octane sulfonic acid, Under existence of metal oxide catalysts, such as silver oxide, or in solvents, such as a non-solvent or a carbon tetrachloride, a cyclohexanone, dioxane, dimethyl sulfoxide, fluoride benzene, a nitrobenzene, mono-glyme, a jig lime, and a TORIGU lime 0-400 degrees C, it is about 25-250 degrees C in temperature preferably, and is a formula. (1) What is necessary is just to make 3 quantification reactions (triazine ring formation reaction) of a fluoride nitril compound perform for about 1 to 200 hours. in addition -- usually -- a catalyst -- formula (1) the 0.01 - 10 mass % extent activity of a nitril compound -- it carries out.

[0070] Formula (12) The triazine compound expressed has three sulfonic groups in 1 molecule, and is useful as intermediate field of a low-molecular electrolyte or a polymer electrolyte.

[0071] Moreover, formula of this invention (1) A fluorine-containing nitril compound is convertible for

the crosslinked polymer containing a sulfonic group by mixing this with the fluorine-containing polymer which has a cyano group in a dinitrile compound or a side chain, and performing a triazine ring formation reaction.

[0072] If the low-molecular electrolyte or polymer electrolyte of the triazine ring content which has the sulfonic group which are obtained by carrying out-like the above is used as a lithium salt mold ($-\text{SO}_3\text{Li}$), it can be used as an electrolyte for lithium rechargeable batteries, and can be suitably used with an acid type ($-\text{SO}_3\text{H}$) as the film of a solid-state polyelectrolyte mold fuel cell, or a polymer for electrode layers.

[0073]

[Example] Hereafter, an example and the example of a comparison explain this invention concretely.

[0074] [Example 1] (1) 346g (one mol) insertion of the $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{COF}$ which are 1450ml and a fluoro formyl compound about diethylether as a solvent is carried out at the 4 opening flask mold reaction container of 3L equipped with the agitator, the thermometer, and the Dewar bottle mold dry ice condensator, and they are after a nitrogen purge and -70 degrees C. It cooled. It is NH_3 there. It is liquefaction NH_3 , cooling with a dry ice condensator. The amidation reaction was performed, while it carried out and 17g (one mol) was dropped at the bottom of churning. NH_3 After dropping termination, it agitated for 0.5 hours, the reaction was completed, and it returned to the room temperature over 2 hours.

[0075] Then, pure water washed reaction rough liquid 3 times, and the separating funnel separated the organic phase. It is $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CONH}_2$ as a white solid-state by distilling off a solvent under reduced pressure, after magnesium sulfate performs moisture clearance of an organic phase. Fluoro amide 303g (0.839 mols) expressed was obtained.

[0076] (2) Subsequently, fluoro amide $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CONH}_2$ obtained by the 4 opening flask mold reaction container of 3L equipped with the agitator, the thermometer, the dropping funnel, and the cooling pipe by dimethylformamide 1200g (1270ml) which is a solvent, and the above 286g (0.834 mols) was inserted in, it considered as the dimethylformamide solution, and this was cooled at 0 degree C. 221g (1.05 mols) of anhydrous trifluoroacetic acid was slowly dropped there over 0.5 hours as a dehydrating agent. Pyridine 167g (2.11 mols) as an acceptor of the acid generated at the time of nitrilizing was further dropped slowly over 1 hour after dropping termination. Reaction temperature was maintained among $2-4$ degrees C in the meantime.

[0077] After dropping termination, it agitated for 0.5 hours, the reaction was completed, and 350g of pure water was added from the tap funnel, and it was left until it became a room temperature. The lower phase of the reaction rough liquid which carried out two-phase separation was isolated preparatively with the separating funnel, distillation was performed after pure-water washing 3 times, and fluoro nitril $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CN}$ 201g (0.583 mols, 70.3% of yield) was obtained.

[0078] Boiling point 89 degrees C, ^{19}F -NMR (CD_3) (2 $\text{C}=\text{O}$ solvent and CFCl_3 criteria, δ ppm) 46.1 (1F, s), -79.8 (1F, dd), -82.8 (1F, d), -83.1 (3F, s), -111.7 (2F, s), -114.4 (1F, m)

[0079] (3) Then, 130g (0.4 mols) of THF 650ml and $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CN}$ obtained by the above was inserted in the 4 opening flask mold reaction container of 2L equipped with the agitator, the thermometer, the three-way cock, and the Dewar bottle mold trap, and it cooled at 0 degree C after the nitrogen purge. It was slowly dropped at the bottom of churning of a water [which is tertiary amine / pyridine 226g (7.15 mols) and 7.2g (0.4 mols) of water] mixed solution, and the hydrolysis reaction was performed there. After dropping termination, it agitated at the room temperature for 3 hours, and the reaction was completed.

[0080] The column was filled up with the ion exchange resin (SK 1BN, the Mitsubishi Chemical make, an ion exchange group: more than a sulfonic group, and ion-exchange-capacity: 5.7 milliequivalent / g desiccation resin particle size : 500-650 micrometers) of an excessive amount, the fixed bed of ion exchange resin was formed, the reaction solution was slowly dipped in this from the upper part, and it was made to flow out of the lower part.

[0081] The reaction solution which carried out ion exchange treatment in this way is inserted in revolution mold concentration equipment (evaporator), evaporation is performed, distillate clearance of

the solvent etc. is carried out by reduced pressure, and it is sulfonic group content fluoro nitril $\text{HOSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CN}$ as concentration liquid. 109.2g (0.338 mols, 84% of yield) was obtained.

[0082] ^{19}F -NMR (CD_3) (2 $\text{C}=\text{O}$ solvent and CFCl_3 criteria, δ ppm) -81.3 (1F, dd), -84.7 (3F, s), -84.9 (1F, dd)-114.8 (1F, m), -119.2 (2F, s)

[0083] LC/MS [[Frit-FAB- (high-speed neutral atomic bombardment method) and collision atom: Xe] M-H] - The strong peak of corresponding $m/z=322$ was detected.

[0084] [Example 1 of a comparison] Methanol 50ml and 21.26g (0.15 mols) of potassium carbonate were inserted in the 200ml three-neck flask mold reaction container equipped with the agitator, the thermometer, the tap funnel, and the cooling pipe, and it cooled at 0 degree C after the nitrogen purge. 10g (0.03 mols) of $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CN}$ (s) compounded in the example 1 was dropped there slowly, and the hydrolysis reaction was performed. After dropping termination, it agitated at the room temperature for 3 hours, and the reaction was completed.

[0085] Although the 46.1 ppm peak of the $-\text{SO}_2\text{F}$ set origin was extinguished and completion of a hydrolysis reaction was suggested when it besides became clear and ^{19}F -NMR analysis was performed about liquid, it turned out that the -114.4 ppm peak which shows existence of a cyano group is also extinguished, and the cyano group has also reacted. That is, in hydrolysis of the fluoro sulfonyl group by alkali like potassium carbonate, it turns out that there is a problem which says that a cyano group will also react simultaneously.

[0086] [Example 2 of a comparison] Without dipping in an ion-exchange resin column, the evaporator was supplied and some reaction rough liquid after the hydrolysis reaction using the reaction intermediate product in an example 1, i.e., a pyridine and water, was condensed. Although superfluous concentrated sulfuric acid was added in concentration liquid and vacuum distillation was performed, it turned out that it has reacted and deteriorated when a distilled cyano group is checked by ^{19}F -NMR measurement. That is, when it changes into a sulfonic acid type using a mineral acid like concentrated sulfuric acid, it turns out that being accompanied by the reaction of a cyano group is not avoided.

[0087]

[Effect of the Invention] Formula which has the sulfonic group and cyano group of this invention in both ends (1) The fluorine-containing nitril compound expressed is new, and useful as intermediate field of the low-molecular electrolyte of triazine ring content, or a polymer electrolyte.

[0088] moreover -- if the approach of this invention is followed -- formula (2) hydrolyzing a fluoro formyl group under existence of tertiary amine by using a compound as starting material, and contacting this on acid type ion exchange resin -- yield -- high -- formula (1) A fluorine-containing nitril compound can be obtained.

[Translation done.]